

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
13 September 2001 (13.09.2001)

PCT

(10) International Publication Number  
**WO 01/66648 A1**

- (51) International Patent Classification<sup>7</sup>: C09B 47/26, C09D 11/00
- (21) International Application Number: PCT/GB01/00570
- (22) International Filing Date: 12 February 2001 (12.02.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
0005299.3 7 March 2000 (07.03.2000) GB
- (71) Applicant (for all designated States except US): AVECIA LIMITED [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): PATEL, Prakash [GB/GB]; P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB). WIGHT, Paul [GB/GB]; P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (74) Agents: MAYALL, John et al.; AVECIA Limited, Intellectual Property Group, Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COMPOUND, COMPOSITIONS AND USE

(57) Abstract: A compound of formula (I):  $\text{Pc-SO}_2\text{-L-SO}_2\text{-Pc}$  wherein each Pc is independently an optionally substituted phthalocyanine group; and L is a divalent linking group; provided that: (i) L is free from halo-s-triazine groups; and (ii) L is not  $\text{-NH-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH-}$ . Inks comprising these compounds, ink jet printer cartridges containing these inks, their use in ink jet printing and substrates printed with these compounds and/or inks.

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COMPOUND, COMPOSITIONS AND USE

This invention relates to dyes, to compositions containing these dyes, to inks, to printing processes, to printed substrates and to ink jet printer cartridges.

5 IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly  
10 when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

Dyes containing a single copper phthalocyanine group and their use in ink jet  
15 printing are known. For example, CI Direct Blue 199 and CI Direct Blue 86 are used as colorants in commercial ink jet printing inks. However, there is a continuing need to provide colorants having superior properties in ink jet printing inks.

According to the present invention there is provided a compound of Formula (1):



Formula (1)

wherein:

each Pc independently is an optionally substituted phthalocyanine group; and  
25 L is a divalent linking group;

provided that:

- (i) L is free from halo-s-triazine groups; and
- (ii) L is not  $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-$ .

Preferably L is a group of Formula (2):



Formula (2)

wherein:

35  $\text{R}^1$  is H, optionally substituted alkyl or optionally substituted aryl; and  
 $\text{L}^1$  is a divalent linking group;

provided that:

- (i) L is free from halo-s-triazine groups; and
- (ii) L is not  $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-$ .

Preferably  $L^1$  comprises one or more carbon atoms and optionally one or more heteroatoms, preferably nitrogen, oxygen and/or sulphur. More preferably  $L^1$  comprises from 1 to 30, especially 2 to 20 carbon atoms and 0 to 20 atoms, especially 1 to 10 atoms selected from oxygen nitrogen and sulphur.

5 In a particularly preferred embodiment  $L^1$  is of Formula (3):



Formula (3)

10 wherein:

- each G independently is optionally substituted alkylene or arylene;
- each X independently is an ester, amide, amine, sulphone, sulfoxide, ether or thioether;
- n is from 1 to 6; and
- 15 p has a value of from 0 to 10;

provided that:

- (i) L is free from halo-s-triazine groups; and
- (ii) L is not  $-NH-CH_2-CH_2-NH-CH_2-CH_2-NH-$ .

20 Preferably each G independently is optionally substituted  $C_{1-6}$  alkylene or optionally substituted phenylene.

Preferably each X independently is a group of formula  $-CO_2-$ ,  $-CONR^2-$ ,  $-NR^2-$ ,  $-O-$ ,  $-SO-$ ,  $-SO_2-$  or  $-S-$  wherein  $R^2$  is H or optionally substituted  $C_{1-4}$  alkyl.

25 Preferably n is 2, 3 or 4, more preferably 2 or 3 especially 2. The value of n may vary from one group of formula  $(C_nH_{2n}-X)$  to another, but preferably n has the same value in all groups of formula  $(C_nH_{2n}-X)$ .

Preferably p has a value of from 0 to 8, more preferably 0 to 6, especially 0,1,2,3,4 or 5.

30 In a preferred embodiment one G is optionally substituted phenylene and the other G is optionally substituted phenylene or optionally substituted  $C_{1-6}$  alkylene and each X independently is  $-O-$ ,  $-SO-$ ,  $-SO_2-$  or  $-NR^2-$  wherein  $R^2$  is H or optionally substituted  $C_{1-4}$  alkyl, n is 2 or 3 and p is 0, 1, 2, 3, 4 or 5.

35 The optional substituents which may be present on G are preferably selected from  $C_{1-4}$  alkyl (especially methyl), halo (especially Cl, F or Br), CN,  $NO_2$ ,  $SO_2F$ , OH,  $-NR^3CONR^3R^4$ ,  $-NR^3R^4$ ,  $-COR^3$ ,  $-COR^3R^4$ ,  $-CO_2R^3$  and  $-SO_2R^3$  wherein  $R^3$  and  $R^4$  are each independently H or optionally substituted  $C_{1-4}$  alkyl or, in the case of  $-CO_2R^3$  and  $-SO_2R^3$ ,  $R^3$  may also be a cation (especially a metal or optionally substituted ammonium cation).

Preferred phthalocyanine groups represented by Pc are each independently selected from metal-free phthalocyanines and metal-containing phthalocyanines. More

preferably phthalocyanine groups represented by Pc are each independently selected from copper phthalocyanine and nickel phthalocyanine.

It is preferred that at least one, and preferably both, of the phthalocyanine groups carries a sulpho substituent. It is also preferred that at least one, and preferably both, of the phthalocyanine groups carries a sulphonamide substituent, preferably of the formula  $\text{SO}_2\text{NR}^5\text{R}^6$  wherein  $\text{R}^5$  and  $\text{R}^6$  are each independently H, optionally substituted alkyl, optionally substituted aryl or  $\text{R}^5$  and  $\text{R}^6$  together with the N atom to which they are attached form an optionally substituted five or six membered ring. Preferably  $\text{R}^5$  and  $\text{R}^6$  are each independently H or optionally substituted  $\text{C}_{1-4}$ -alkyl, especially H or methyl.

It is especially preferred that at least one of the phthalocyanine groups carries a sulpho substituent and a sulphonamide substituent of the formula  $\text{SO}_2\text{NR}^5\text{R}^6$  wherein  $\text{R}^5$  and  $\text{R}^6$  are as hereinbefore defined.

The optional substituents which may be present on  $\text{R}^5$  and  $\text{R}^6$  are preferably each independently selected from sulpho, carboxy, phosphato, hydroxy and amino.

Preferably the compounds described herein are water-soluble.

Compounds of the type as herein described may be prepared by a process comprising condensing at least two molar equivalents of a phthalocyanine compound carrying a group of formula  $-\text{SO}_2\text{Z}$ , wherein Z is a labile group, with a divalent linking group reactive towards  $-\text{SO}_2\text{Z}$  groups. For example diamines of formula  $\text{HNR}^1-\text{L}^1-\text{R}^1-\text{NH}$ , wherein  $\text{L}^1$  and each  $\text{R}^1$  independently are as defined above. Alternately the compounds may be prepared by condensing a phthalocyanine compound carrying a substituent of the formula  $-\text{SO}_2\text{NR}^1-\text{L}^1-\text{NH}^1\text{H}$  with a phthalocyanine compound carrying a substituent of the formula  $-\text{SO}_2\text{Z}$ , wherein Z is a labile group and  $\text{L}^1$  and  $\text{R}^1$  independently are as defined above. Typical labile groups are halogens, especially chloro.

According to a second aspect of the present invention there is provided a composition comprising a compound of Formula (1) and a liquid medium.

Preferred compositions comprise:

(a) from 0.01 to 30 parts of a compound of Formula (1); and

(b) from 70 to 99.99 parts of a liquid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates which may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and an organic solvent and an organic solvent free from water.

When the medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C<sub>1-6</sub>-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C<sub>1-4</sub>-alkyl ethers of diols, preferably mono-C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)-ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoalkylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-soluble organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkyl ethers of diols, more preferably mono-C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Although not usually necessary, further colorants may be present in the liquid medium to modify the shade and performance properties of the composition. Examples of such colorants include C.I.Direct Yellow 86, 132, 142 and 173; C.I.Direct Blue 199, and 307; C.I.Food Black 2; C.I.Direct Black 168 and 195; C.I. Acid Yellow 23; and any of the dyes used in ink jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International. Addition of such further dyes can increase overall solubility leading to less clogging (nozzle blockage) for the resultant ink.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50° to 125°C. The organic solvent  
5 may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH<sub>2</sub>Cl<sub>2</sub>; and ethers, preferably diethyl ether; and mixtures thereof.

10 When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include C<sub>1-4</sub>-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and/or an alcohol  
15 (especially a C<sub>1-4</sub>-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium  
20 to be selected which gives good control over the drying characteristics and storage stability of the ink.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

Preferably the composition has been filtered through a filter having a mean pore  
25 size below 10µm, more preferably below 3µm, especially below 2µm, more especially below 1µm. This filtration removes particulate matter which could otherwise block the fine nozzles found in many ink jet printers.

The compositions preferably have a total concentration of divalent and trivalent metal ions other than those associated with the phthalocyanine below 1000, more  
30 preferably below 100, especially below 20, more especially below 10 parts per million by weight relative to the total weight of ink. Pure compositions of this type may be prepared by using high purity ingredients and/or by purifying the composition after it has been prepared. Suitable purification techniques are well known, e.g. ultrafiltration, reverse osmosis, ion exchange and combinations thereof.

35 The liquid medium may also contain further components which are conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogation reducing additives and surfactants which may be ionic or non-ionic.

The composition may be an ink, especially an ink-jet printing ink, or a liquid dye concentrate which is used to prepare inks. The concentrates are useful as a means for transporting colorant and so minimising costs associated with drying the dye and transporting excess liquid.

5       The compounds of Formula (1) have attractive, strong cyan shades and are valuable colorants for ink-jet printing inks. They benefit from a good balance of solubility, storage stability and fastness to water and light. In particular the compounds of Formula (1) are stable to oxidative gases such as ozone, nitrous oxide, NO and NO<sub>2</sub>. The compounds of Formula (1) particularly benefit from their stability to ozone.

10       A third aspect of the invention provides a process for printing an image on a substrate comprising applying a composition according to the second aspect of the current invention to the substrate by means of an ink jet printer.

15       The ink jet printer preferably applies the composition to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the composition in a reservoir by means of a resistor adjacent to the orifice, thereby causing the composition to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printer, the oscillation of a small crystal  
20       causes ejection of the composition from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass more preferably paper, an overhead projector slide or a textile material, especially paper.

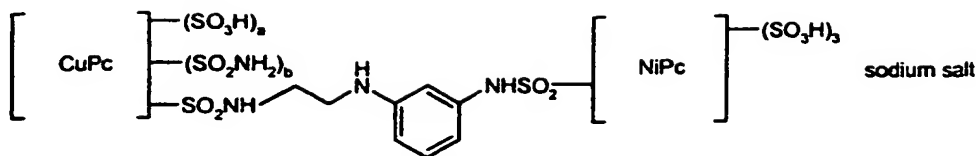
Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character.

25       A fourth aspect of the present invention provides a substrate, especially paper, an overhead projector slide, a textile material, a plastic, glass and metal, printed with a composition, a compound or by means of a process as hereinbefore defined.

30       A fifth aspect of the present invention provides an ink jet printer cartridge comprising a chamber and a composition wherein the composition is in the chamber and the composition is as described according to the second aspect of the present invention.

A sixth aspect of the invention is a method for the coloration of a substrate which comprises applying thereto a compound according to the first aspect of the invention.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

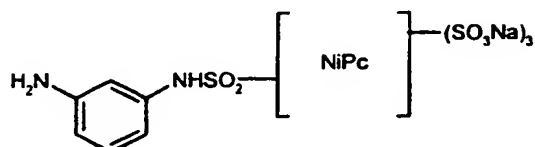
Example 1Preparation of:

5

wherein the sum of a + b is 3.

Step 1:Preparation of:

10



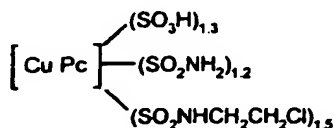
15

This compound was prepared by the method described in EP471456A1, Example 1 first two paragraphs.

Step 2:

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The product of step 1 (10.6g) was stirred in water (600ml) at room temperature and pH 9-10. CI Reactive Blue 25 (11.3g) was added stepwise and the pH maintained at 9-10 using 2M NaOH.



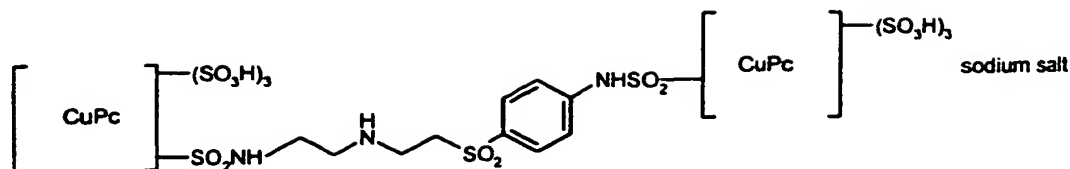
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C.I. Reactive Blue 23

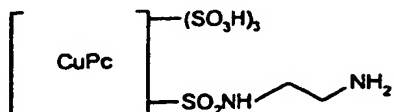
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The mixture was heated at 70°C for 4hr, cooled and the pH lowered to 7 with concentrated HCl. The precipitated product was filtered, washed with 0.5M HCl, converted to the sodium salt, desalinated and dried to give the product (18.7g) having absorbance maxima at 615 and 660 nm. Analysis by mass spectroscopy revealed multiple species of which the title product was the major component.



Example 2Preparation of:

5

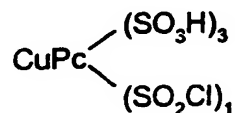
Step1:Preparation of:

10

Sulphuric acid (9.4g) was added to chlorosulphonic acid (192g) followed by copper phthalocyanine (38.4g) below 60°C. The reaction mixture was heated at 130-140°C for 2hr, cooled and drowned out into ice/water (480g). The precipitated solid was filtered-off and washed with 0.5M HCl (600ml). The solid was added stepwise to a stirred solution of ethylene diamine (4g) in ice/water (340g). The reaction mixture was then heated at 40°C, pH7-8 for 2hr, cooled and the pH was lowered to 3-4 using concentrated HCl. The precipitate was filtered-off and washed with saturated brine to give the compound shown above.

15

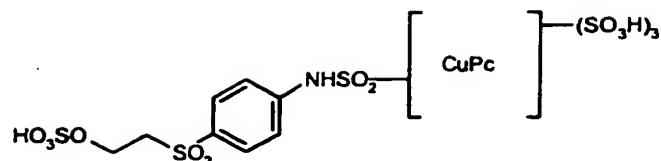
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Step 2:Preparation of:

25

Copper phthalocyanine (115g) was added in portions to stirred chlorosulphonic acid (317 ml) and concentrated sulphuric acid (147 ml). The mixture was heated to 140°C for 3 hours and then cooled to room temperature. This mixture was then poured onto a stirred mixture of ice (1 kg), water (200 ml), concentrated hydrochloric acid (44 ml) and sodium chloride (40g). The precipitated product was collected by filtration at reduced pressure to obtain a paste of  $\text{CuPc}(\text{SO}_3\text{H})_3(\text{SO}_2\text{Cl})_1$  (817.8 g) which was used directly in the next step.

30

**Step 3****Preparation of:**

5

The product of step 2 was added to a mixture of p-aminobenzenesulphatoethyl sulphone (133g) in water (700 ml) at pH 5.2 (adjusted by adding 15 % aqueous NaOH). The mixture was stirred at pH 5.2 and room temperature for 3 hours. Sodium chloride (20% w/v) was added to the mixture which was stirred for 15 minutes and the pH of the mixture was adjusted to 1.0 with concentrated hydrochloric acid. The resultant precipitate was collected by filtration at reduced pressure and washed with ice-cold brine (10%) and dried under reduced pressure to obtain 688 g of product.

10

**Step 4:**

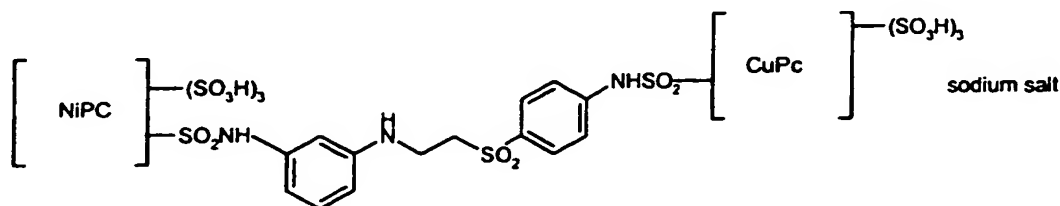
15

The product of step 1 (23g) was added portion-wise to a stirred solution of the product of step 3 (148 g, 28% strength) in water (1000ml) at pH 9-10 and room temperature. The mixture was heated at 70°C for 4.5 hr at pH 9-10 and then cooled and the pH lowered to pH 3-4 using concentrated HCl. The precipitated solid was filtered-off, washed with 0.5M HCl, converted to the sodium salt, desalinated and dried to give the product (62g) having absorbance maxima at 625 and 665 nm. Analysis by mass spectroscopy revealed multiple species of which the title product was the major component.

20

**Example 3**

25

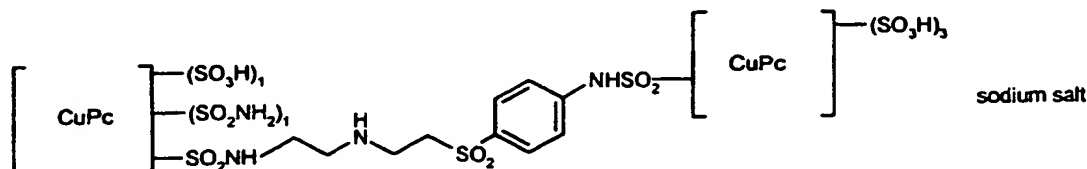
**Preparation of:**

30

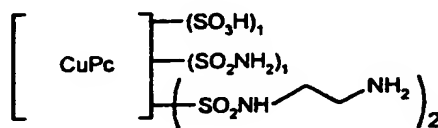
The product of Example 1, Step 1(20g) was added to a solution of the product of Example 2 Step 3 (92g, 28% strength) in water (1000ml) at pH 9-10. The mixture was heated at 70°C for 4hr, cooled and the pH lowered to 3-4 with concentrated HCl. The precipitate was filtered-off, washed with 0.5M HCl, converted to the sodium salt,

desalinated and dried to give the product as a solid (30g) having absorbance maxima at 625 and 660 nm. Analysis by mass spectroscopy revealed multiple species of which the title product was the major component.

5 Example 4  
Preparation of:



10 Step 1:  
Preparation of:



15 Copper phthalocyanine (115.2g) was added to chlorosulphonic acid (308ml) below 50°C and then heated at 140°C for 3hr. The mixture was cooled to 40°C and phosphorous trichloride (52g) was added over 1hr below 50°C. The mixture was then heated at 90°C for 1.5 hr, cooled and poured into ice/water (1400ml). The solid was filtered-off and washed with 0.5M HCl (2000ml). This was added to a stirred solution of chloroethylamine hydrochloride (46.6g) in water (1000ml) at 0°C and the pH was raised to 7-8 with 2M ammonium hydroxide, stirred at 0°C for 1 hr and at 40°C for 0.5 hr. The reaction mixture was cooled, the pH lowered to 1.5 with concentrated HCl and the precipitate was filtered-off and washed with 0.5M HCl. This solid was then stirred in water (2000ml) and concentrated ammonia (500ml) was added. The reaction was then heated at 60-70°C for 4 hr, cooled and the pH adjusted to 4 with concentrated HCl. Precipitated product was filtered-off, washed with water and acetone and dried to give the intermediate (180g) shown above.

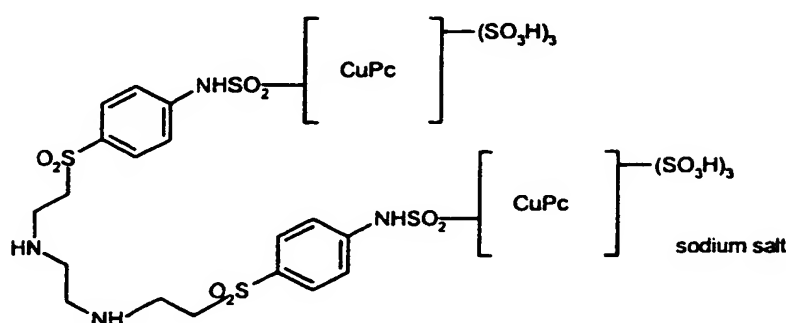
25 Step 2:

30 The product of Step 1 (18g) was added to the product of Example 2, Step 3 (130g, 28% strength) in aqueous (2000ml) pH 9-10 solution. The reaction mixture was heated at 70°C for 5 hr, cooled and the pH was lowered to 3-4 with concentrated HCl. The resultant precipitate was filtered off, washed with 0.5M HCl, converted to the sodium salt, desalinated and dried to give the product (31g) having absorbance maxima at 625 and

665 nm. Analysis by mass spectroscopy revealed multiple species of which the title product was the major component.

### Example 5

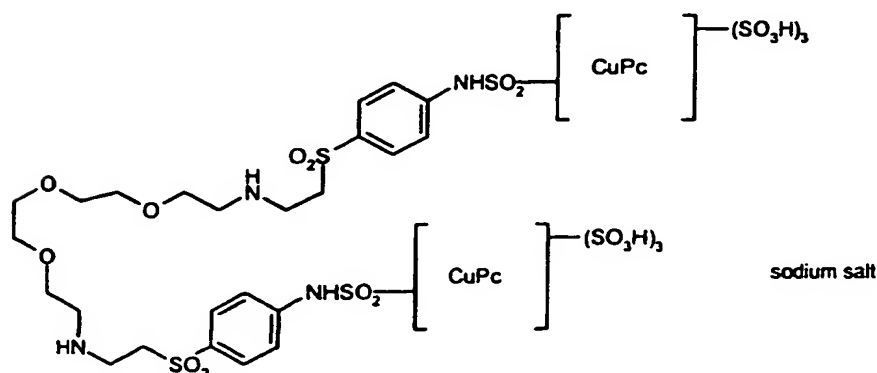
#### 5 Preparation of:



10 The compound from Example 2, Step 3 (90g, 28%) was dissolved in water (1000ml). Ethylene diamine (0.6g) was added and the pH was maintained at 9-10 by the addition of 2M NaOH. The reaction mixture was stirred at room temperature for 1 hr and then at 70°C for 2.5 hr, cooled and the pH lowered to 2-3 with concentrated HCl. The precipitate was collected by filtration, converted to the sodium salt, desalinated and dried to give the product (21.7g) as a solid having absorbance maxima at 630 and 665 nm. Analysis by mass spectroscopy revealed multiple species of which the title product was the major component.

### Example 6

#### 20 Preparation of:



25 The compound shown in Example 2, Step 2 (90g, 28% strength) was dissolved in water (1000ml). 4,7,10-trioxatridecylamine (2.2g) was added and the pH was maintained

at 9-10 by the addition of 2M NaOH. The reaction mixture was stirred at room temperature for 1 hr and then at 70°C for 2.5 hr, cooled and pH lowered to 2-3 with concentrated HCl. The precipitate was filtered-off, converted to the sodium salt, desalinated and dried to give the product (23g) as a solid having absorbance maxima at 630 and 665 nm. Analysis by mass spectroscopy revealed multiple species of which the title product was the major component.

#### Example 7

##### Preparation of inks

Inks were prepared by dissolving 3 parts (weight by weight) of the dye in a stock solution of 5 parts 2-pyrrolidone, 5 parts thiodiglycol, 2 parts Surfynol 465 (a surfactant commercially available from Air Products Inc.) and 85 parts distilled water with the addition of concentrated sodium hydroxide to give a pH of 8.5 to 9. The resultant inks were as follows:

Ink (1) contained Dye (1)  
Ink (2) contained Dye (2)  
Ink (3) contained Dye (3)  
Ink (4) contained Dye (4)  
Ink (5) contained Dye (5)  
Ink (6) contained Dye (6)  
Comparative Ink contained Comparative Dye

The Comparative Dye was C.I. Direct Blue 199, a copper phthalocyanine dye obtained from Avecia Limited.

Each ink was filtered through a 0.45µm filter and put into one chamber of a Canon trichamber inkjet cartridge.

"Surfynol" is a registered trade mark of Air Products Inc.

##### Ink Jet Printing

Inks 1 and 2 were then ink jet printed onto each of the substrates shown in Tables A to F using a Canon 4300 IJ printer, the following results were obtained:

The CIE colour co-ordinates of each print (a, b, L, Chroma) were measured using a Xrite 983 Spectrodensitometer with 0°/45° measuring geometry with a spectral range of 400-700nm at 20nm spectral intervals, using illuminant C with a 2° (CIE 1931) observer angle and a density operation of status T. No less than 4 measurements were taken diagonally across a solid colour block on the print with a size greater than 10mm x 10mm.

The OD is the optical density of the printed paper, as measured by a Xrite 983 Spectrodensitometer

Table A: Ink 1

Substrate	OD	L	a	b	Hue	Chroma
Canon HG201 - High Gloss Film	2.224	51	-38	-36	224	53
SEC Photopaper	1.845	47	-31	-36	229	47
SEC Coated 720dpi Photo quality Ink Jet paper	1.167	58	-27	-33	231	43
Xerox 4024	1	59	-24	-27	228	37

Table B: Ink 2

Substrate	OD	L	a	b	Hue	Chroma
Canon HG201 - High Gloss Film	2.254	55	-31	-48	237	57
SEC Photopaper	1.882	51	-24	-48	244	54
SEC Coated 720dpi Photo quality Ink Jet paper	1.224	59	-23	-43	241	49
Xerox 4024	1.009	61	-22	-36	239	43

5

Table C: Ink 3

Substrate	OD	L	a	b	Hue	Chroma
Canon HG201 - High Gloss Film	2.219	54	-42	-35	220	54
SEC Photopaper	1.845	50	-34	-35	226	49
SEC Coated 720dpi Photo quality Ink Jet paper	1.194	59	-31	-32	226	44
Xerox 4024	0.975	61	-27	-26	224	37

Table D: Ink 4

Substrate	OD	L	a	b	Hue	Chroma
Canon HG201 - High Gloss Film	2.282	55	-30	-48	238	57
SEC Photopaper	1.908	50	-24	-47	242	53
SEC Coated 720dpi Photo quality Ink Jet paper	1.261	58	-23	-43	241	49
Xerox 4024	1.02	61	-22	-36	238	42

Table E: Ink 5

Substrate	OD	L	a	b	Hue	Chroma
Canon HG201 - High Gloss Film	2.041	58	-34	-46	234	57
SEC Photopaper	1.814	53	-29	-45	237	54
SEC Coated 720dpi Photo quality Ink Jet paper	1.162	62	-26	-41	237	49
Xerox 4024	1.001	62	-25	-35	235	43

Table F: Ink 6

Substrate	OD	L	a	b	Hue	Chroma
Canon HG201 - High Gloss Film	2.167	56	-37	-43	229	56
SEC Photopaper	1.87	52	-28	-46	239	54
SEC Coated 720dpi Photo quality Ink Jet paper	1.213	60	-27	-40	236	49
Xerox 4024	0.991	62	-24	-34	234	42

Further Inks

5 The inks described in Tables I and II may be prepared wherein the Dye described in the first column is the Dye made in the above example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in Table I and II:

PG = propylene glycol  
DEG = diethylene glycol  
10 NMP = N-methyl pyrrolidone  
DMK = dimethylketone  
IPA = isopropanol  
MEOH = methanol  
2P = 2-pyrrolidone  
15 MIBK = methylisobutyl ketone  
P12 = propane-1,2-diol  
BDL = butane-2,3-diol  
CET = cetyl ammonium bromide  
PHO =  $\text{Na}_2\text{HPO}_4$  and  
20 TBT = tertiary butanol  
TDG = thiodiglycol



TABLE I

Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
3	10.0	85	3		3	3				5	1	
4	2.1	91		8								1
5	3.1	86	5					0.2	4			5
6	1.1	81			9		0.5				9	
1	2.5	60	4	15	3	3			6	10	5	4
2	5	65		20					10			
3	2.4	75	5	4		5				6		5
1	4.1	80	3	5	2	10		0.3				
1	3.2	65		5	4	6			5	4	6	5
1	5.1	96								4		
1	10.8	90	5						5	4		
1	10.0	80	2	6	2	5					4	
4	1.8	80		5					1		15	
1	2.6	84			11						5	
1	3.3	80	2			10				2		6
1	12.0	90				7	0.3		3			
4	5.4	69	2	20	2	1					3	3
1	6.0	91			4						5	

TABLE II

Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					5	
1	9.0	90		5						1.2		5
6	1.5	85	5	5		0.15	5.0	0.2				
1	2.5	90		6	4					0.12		
1	3.1	82	4	8		0.3						6
1	0.9	85		10					5	0.2		
1	8.0	90		5	5			0.3				
5	4.0	70		10	4				1		4	11
6	2.2	75	4	10	3				2		6	
3	10.0	91			6						3	
1	9.0	76		9	7		3.0			0.95	5	
1	5.0	78	5	11							6	
1	5.4	86			7						7	
5	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	
1	2.0	90		10								
1	2	88						10				
1	5	78			5			12			5	
1	8	70	2		8			15			5	
1	10	80						8			12	
2	10	80		10								

CLAIMS

1. A compound of Formula (1):



Formula (1)

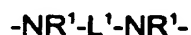
wherein:

- each Pc is independently an optionally substituted phthalocyanine group; and  
10 L is a divalent linking group;

provided that:

- (i) L is free from halo-s-triazine groups; and  
(ii) L is not  $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-$ .

- 15 2. A compound according to claim 1 wherein L is a group of Formula (2):



Formula (2)

20 wherein:

- $\text{R}^1$  is H, optionally substituted alkyl or optionally substituted aryl; and  
 $\text{L}^1$  is a divalent linking group comprising from 1 to 30 carbon atoms and 0 to 20  
atoms selected from oxygen nitrogen and sulphur.

25 provided that:

- (i) L is free from halo-s-triazine groups; and  
(ii) L is not  $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-$ .

- 30 3. A compound according to claim 1 and claim 2 wherein  $\text{L}^1$  is of Formula (3):



Formula (3)

35

wherein:

- each G independently is optionally substituted alkylene or arylene;  
each X independently is an ester, amide, amine, sulphone, sulfoxide, ether or  
thioether;

n is from 1 to 6; and  
p has a value of from 0 to 10.

provided that:

- (i) L is free from halo-s-triazine groups; and  
(ii) L is not -NH-CH<sub>2</sub>-CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH-.

4. A compound according to any one of the preceding claims wherein the phthalocyanine groups are each independently selected from metal-free phthalocyanines and metal containing phthalocyanines.

5. A compound according to any one of the preceding claims wherein the phthalocyanine groups are each independently selected from copper phthalocyanine and nickel phthalocyanine.

6. A compound according to any one of the preceding claims wherein at least one of the phthalocyanine groups carries a sulpho substituent.

7. A compound according to any one of the preceding claims wherein at least one of the phthalocyanine groups carries a sulphonamide substituent.

8. A compound according to any one of the preceding claims wherein at least one of the phthalocyanine groups carries a sulpho substituent and a sulphonamide substituent of the formula SO<sub>2</sub>NR<sup>5</sup>R<sup>6</sup> wherein R<sup>5</sup> and R<sup>6</sup> are each independently H, optionally substituted alkyl, optionally substituted aryl or R<sup>5</sup> and R<sup>6</sup> together with the N atom to which they are attached form an optionally substituted five or six membered ring.

9. A compound according to any one of the preceding claims which is water-soluble.

10. A process for preparing a compound according to any one of the preceding claims comprising condensing two molar equivalents of a phthalocyanine compound carrying a group of formula -SO<sub>2</sub>Z with a diamine of formula HNR<sup>1</sup>-L<sup>1</sup>-R<sup>1</sup>-NH wherein Z is a labile group and L<sup>1</sup> and each R<sup>1</sup> independently are as defined in claim 2.

11. A process for preparing a compound according to any one of claims 1 to 9 wherein a phthalocyanine compound carrying a substituent of the formula -SO<sub>2</sub>NR<sup>1</sup>-L<sup>1</sup>-NH<sup>1</sup>H is condensed with a phthalocyanine compounds carrying a substituent of the formula -SO<sub>2</sub>Z, wherein Z is a labile group and L<sup>1</sup> and R<sup>1</sup> independently are as defined in claim 2.

12. A composition comprising a compound according to any one of claims 1 to 9 and a liquid medium.

13. A composition according to claim 12 which is an ink or liquid dye concentrate.
- 5 14. A process for printing an image on a substrate comprising applying a composition according to claim 12 to the substrate by means of an ink jet printer.
- 10 15. A paper, an overhead projector slide, a textile material, a plastic, glass and metal printed with a composition according to claim 12, with a compound according to any one of claims 1 to 9 or by means of a process according to claim 14.
16. An ink-jet printer cartridge comprising a chamber and a composition wherein the composition is in the chamber and the composition is as described in claim 12.
- 15 17. A method for the coloration of a substrate which comprises applying thereto a compound according to any one of claims 1 to 9.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/00570

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09B47/26 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 69, no. 16, 14 October 1968 (1968-10-14) Columbus, Ohio, US; abstract no. 60042z, XP002166210	1-10,12, 17
Y	abstract & CZ 121 235 A (CHMATAL VLADIMIR ET AL) 15 December 1966 (1966-12-15)	1-17
X	US 3 325 511 A (T. E. LESSLIE, W.J. BRYAN) 13 June 1967 (1967-06-13)  column 2, line 45 - last line; examples 19-34	1,2,4-6, 9,10,12, 17
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-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

27 April 2001

Date of mailing of the international search report

25/05/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl  
Fax: (+31-70) 340-3016

Authorized officer

Dauksch, H

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 01/00570

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